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THE INFLUENCE OF IMPURITIES ON THE FORMATION OF SINGLE-CRYSTAL FILMS

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I.   INTRODUCTION

In order to understand the formation of single-crystal films one has

to find out why crystals prefer specific mutual orientations. Volmer and

Weber[1] suggested a reason for this more than forty years ago. They pointed

out that the energy of the interface between two crystals has minima for

specific mutual orientations. When a crystal is formed on the surface of

another crystal the work of formation of the nucleus is smallest when the

nucleus has an orientation with minimum interfacial energy, and, therefore,

the nucleation probability for crystals with such an orientation is highest.

The only attempt[2] to apply Volmer and Weber's[1] idea quantitatively to the

orientation problem was only partially successful. The theoretical part of

this attempt was based on an analysis of the influence of the interfacial

energy on size and shape of a crystal[3] and on a generalization from the

homogeneous case to the heterogeneous case[2] of the derivation of the nucle-

ation probability as given by Zeldovich (see Frenkel[4]). The experimental

system chosen contained crystals with several specific orientations (i) so

that not only their number (N_i) but also their size (g_i) and shape (ξ_i)

could be compared with theory. The comparison of theory and experiment

showed that only part of the qualitative predictions of the theory agreed

with experiment, and that quantitative agreement was poor. In retrospect

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this is not too surprising: only three points on the $F_i(t)$ curves

($F_i = N_i$, g_i, ξ_i; t = deposition time) were taken; extrapolation to t → 0

had to be done from relatively thick films and the vacuum and crystal

quality was poor. Work during the past ten years in many laboratories

has shown (a) that secondary processes such as coalescence can have consid-

erable influence on $F_i(t)$ so that a comparison between an extrapolation $F_i(t)$

to t → 0 with nucleation theory may not be meaningful (see e.g., ref. 5),

and (b) that several parameters have considerable influence on the crystal

orientation but are not explicitly included in the theory. The most sig-

nificant of these parameters are impurities. This paper is concerned with

investigations of the influence of impurities on epitaxy, i.e., on the

orientation of crystals grown on the surface of another crystal. The sys-

tems to be discussed are f.c.c. metals on alkali halides (mainly Au on NaCl).

The following notations will be used to describe the observed orienta-

tions in the deposited film "D" on the substrate "S".

1. (100) stands for the parallel epitaxial growth: $(100)_D \parallel (100)_S$,
$[010]_D \parallel [010]_S$.

2. (111) stands for $(111)_D \parallel (100)_S$, $[01\bar{1}]_D \parallel [01\bar{1}]_S$, $[0\bar{1}1]_S$, $[011]_S$,
$[0\bar{1}\bar{1}]_S$, $[001]_S$, $[00\bar{1}]_S$, $[010]_S$, or $[0\bar{1}0]_S$.

3. TEM stands for transmission electron microscopy.

4. TED stands for transmission electron diffraction.

In the interest of brevity only the major orientations are mentioned.

For a detailed listing see ref. 6. Films will be referred to as "thin"

when the individual crystals (particles) are well separated and it is be-

lieved that coalescence has not played a major role in their formation.

These films are normally less than 5 Å average film thickness. "Thick"

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films are films in which major coalescence has already occurred. They may be discontinuous or continuous.

II. EXPERIMENTAL·

Two separate systems are being used in this laboratory to study the growth of f.c.c. metals on alkali halides. Both are all stainless steel, ion-pumped, and have base pressures in the 10^{-10} torr range. One system is a high energy reflection electron diffraction camera (UHV-RHEED) which allows _in situ_ observation of the film growth.[6,7] The other is a large volume evaporation chamber and has a specimen holder arrangement enabling simultaneous deposition on three substrates. Vacuum cleavage is possible in both systems. A Sloan quartz crystal rate monitor was used during depositions in the evaporation chamber and was placed in the specimen position of the UHV-RHEED system for calibration. Au of 99.9999% quoted purity and optical grade Harshaw NaCl was used except where noted. The films prepared in these systems were backed with carbon after removal. Standard techniques were used to prepare specimens for electron microscopy.

III. BULK IMPURITIES

When the bulk of a crystal contains impurities, they will generally also be present on its surface. For example, the Ca, Fe, and Si impurities in MgO crystals have been suggested as the cause for the observation of Robins and Rhodin[8] that Au crystals form on MgO cleavage planes only at defects. They noted that with increasing deposition time the number of particles approached one and the same constant value N_{max} independent of substrate temperature (from 209° to 381°C) and that N_{max} was of the same

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order to magnitude as the Fe and Si surface density expected from the bulk concentration. This suggests that nucleation occurred only at impurities. The question arises: what is the influence of these impurities on the particle orientation? To answer this question one has to compare the orientation of films grown on surfaces of doped crystals with those on undoped crystals. We have done this by studying the growth of Au on clean and Ca-doped NaCl* (.2 mole percent $CaCl_2$). The results are as follows: The orientation of films on vacuum-cleaved surfaces of doped crystals is similar to that on undoped crystals. On the air-cleaved surfaces, however, a major difference is observed between doped and undoped crystals. On the doped crystal the (111) is dominant, on the undoped the (100). Figure 1 shows a comparison of thin films on air-cleaved surfaces of doped and undoped specimens. A thick film deposited on a doped specimen is predominantly (111) on both air- and vacuum-cleaved surfaces. Observations of the behavior of UHV-cleaved surfaces thus show that Ca alone has little influence on the particle orientation, but that the interaction of a Ca-doped surface with atmosphere drastically changes the particle orientation. This is not surprising for $CaCl_2$ is highly hygroscopic so that a much stronger interaction between water vapor and a Ca-doped surface than with an undoped surface is to be expected. This difference in surface condition is also reflected in the particle density and distribution on air-cleaved surfaces (see Fig. 1b, d). On the vacuum-cleaved surfaces particle density and distribution are very similar both on doped and undoped surfaces.

We conclude that .2% Ca doping in NaCl per se has little influence on particle orientation, density, and distribution under our experimental conditions but that the dopant strongly influences the film growth on air-cleaved surfaces indirectly by modifying the interaction between water vapor and the crystal surface.

IV. SURFACE IMPURITIES

Impurities which do not exist in the bulk may be present on the surface
if the surface is exposed to an environment in which a surface adsorption or
reaction layer can be formed. Such a surface layer may have a profound influ-
ence on the film formation. Ino et al.[9] discovered significant differences in
the orientation of some f.c.c. films deposited simultaneously on air- and
vacuum-cleaved NaCl surfaces. They attributed these differences to the forma-
tion of an impurity layer on the air-cleaved surface. The nature of this
impurity layer is still a matter of controversy. The models proposed include
water multilayers,[10] a carbonate layer,[11] and a hydrate-like surface layer.[12,13]
We accept here the last model with the following modifications: (1) the sur-
face layer may contain some CO_2 and CO, and (2) hydrolysis may have occurred
in the hydrate-like layer at the deposition temperature so that the surface
layer contains OH ions. The first model, which predicts layer by layer de-
sorption upon heating in vacuum is not supported by our recent experimental
results.[14]

The surface layer can, however, be removed by sufficiently long vacuum
heat treatment at sufficiently high temperatures. This influence of pre-
heating on crystal orientation was noted 30 years ago by Shirai.[15] Recent
work[7,16] has verified the preheating effect. If the surface layer formed
by cleaving in air is not removed before deposition of the f.c.c. metal film,
the orientations of continuous films differ drastically from those on vacuum-
cleaved surfaces. Ino et al.[9] found that at 5-9·10[-5] torr epitaxy occurred
at lower temperatures on vacuum-cleaved surfaces than on air-cleaved NaCl
surfaces. As we will see later, this effect is mainly due to the high

residual gas pressure. At low residual gas pressure ($2 \cdot 10^{-8}$ - $5 \cdot 10^{-7}$ torr) in a baked vacuum system, Ino et al.[9] found no difference in the orientation of continuous Au, Ag, and Cu films on air- and vacuum-cleaved surfaces. Later experiments[6,7,17] of simultaneous depositions on air- and vacuum-cleaved surfaces, however, revealed important differences between air- and vacuum-cleaved surfaces also at low residual gas pressures. The difference was just opposite to that found at high residual gas pressures, i.e., no epitaxy on the vacuum-cleaved surface, good epitaxy on the air-cleaved surface. The discrepancy between Ino's and the later results can be easily explained by the severe bake-out of his vacuum system, which very likely removed the surface layer on the air-cleaved surface.

Two mechanisms have been proposed to explain the orientation difference between coalesced films on air- and vacuum-cleaved surfaces in UHV. Both are based on the observation that the surface condition has no drastic influence on the initial orientation of very thin films.[6,18] The first mechanism, suggested by Matthews,[18] assumes that the growth rate of (111) crystals is much larger than that of (100) crystals. Then if a very thin film contains both (111) and (100) particles, and if the particles are far apart initially, the (111) particles will become increasingly larger than the (100) particles with increasing film thickness. When coalescence occurs the smaller (100) particles recrystallize by diffusion or are converted into twins of the large (111) particles. The result is a predominantly (111) film. If the initial particle density is high, the (111) particles are not larger than the (100) particles when coalescence occurs. Matthews' mechanism states that in this case the (100) will prevail. We have suggested another mechanism[19] which attributes the difference between

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films on air- and vacuum-cleaved surfaces to a difference in the coalescence process. It assumes that upon coalescence the resulting particle assumes a configuration of lowest free surface and interfacial free energy attainable without considerable diffusion. If the surface free energy does not change upon coalescence, and if the interaction between particle and substrate is weak ("poor wetting"), the resulting particle will have a tendency to be bound by {111} planes including the contact plane with the substrate. Thus the film tends towards a (111). If, however, during coalescence reaction between particle and substrate can occur, and if this leads to a lowering of the (100) surface and interfacial energy, the average film orientation will tend towards a (100). In applying this mechanism to the growth of Au on NaCl it is assumed that the air-cleaved surface--containing probably NaOH and Na_2CO_3 in addition to NaCl--can react with Au during coalescence. These impurities are not present on the clean surface and reaction with Au does not occur. The relative merits of these two models may be judged from the following observations: (1) Au films deposited on vacuum-cleaved KCl have initially the same small particle density and the same orientation as films deposited simultaneously on vacuum-cleaved NaCl, but develop with increasing film thickness perfect epitaxy.[6,20,21] (2) Thick Ag films on both vacuum- and air-cleaved (rel. humidity < 50%) KCl surfaces are predominantly (111) although the initial particle density on the air-cleaved surface is much higher than on the vacuum-cleaved surface.[6] (3) Most of the "(111) particles" in Au films on vacuum-cleaved NaCl do not have the flat shape assumed in Matthews' argument for the higher growth rate of (111) crystals, but are multiple twinned particles.[22,23]

Observations (1) and (2) are incompatible with the Matthew's mechanism, and observation (3) eliminates its basis. Our mechanism, however, is compatible with all three observations if the following assumptions are made: (a) Au can react at the deposition temperature during coalescence with clean KCl but not with clean NaCl, (b) the reaction products reduce the surface and interfacial energy of the (100) plane, and (c) Ag does not react with air- or vacuum-cleaved KCl under our experimental conditions. With these assumptions and keeping in mind the magnitude of the twin-boundary energy of the various materials, the change in film orientation with increasing film thickness both on air- and vacuum-cleaved surfaces can be accounted for. This is discussed elsewhere[19] in more detail. We want to point out that this mechanism depends critically on the nature of the surface structure of the Au (100) surface which is still a matter of considerable controversy. Some observers, including us,[20,24,25] attribute the complex diffraction patterns observed from Au (100) surfaces to impurity effects, while others[26,27] ascribe them to the clean surface. In order to explain the observations mentioned above, we have to assume that the impurity in our case is Na or K and that the "5x1" diffraction pattern is due to double scattering between a very thin Na (or K) deficient surface layer with $NaAu_2$ structure and the (100) Au substrate.[28]

The influence of the surface layer on the film orientation is complicated by the fact that--at least in some systems--it depends on the degree to which the surface was modified by the air exposure. This has been demonstrated by Bethge and Krohn[29] who showed that epitaxial Ag films could be grown on air-cleaved NaCl exposed to a humidity greater than 75% but not with exposure to less than 60%, a result which we have confirmed in ultrahigh vacuum.

In conclusion, the presence of an impurity layer as produced by H_2O or air exposure on alkali halide surfaces seems to have little influence on the crystal orientation in very thin films. It can, however, strongly influence the coalescence process of certain materials. This can be explained qualitatively by the influence of impurities on the surface and interfacial energy. A complete understanding must wait for more precise information on the nature and structure of the surfaces of f.c.c. metals, especially the (100) surface, and their reactions with alkali compounds.

V. RESIDUAL GAS IMPURITIES

As indicated in the previous section, the residual gas in the evaporation system can have a strong influence on the growth of single crystal films. Table I lists typical relative peak heights in the residual gas mass spectra of all stainless steel ion-pumped systems in the baked and unbaked condition. Probably the most important feature for our considerations is that the water peak which accounts for the larger part of the residual gas in the unbaked system is entirely absent in the baked system. In view of Table I it is not surprising that major differences in the results obtained in baked and unbaked systems have been reported.[9,30,31] However, there are also large discrepancies between different authors working with unbaked systems, i.e., with systems containing mainly H_2O vapor as residual gas. The lowering of the epitaxial temperature by vacuum cleaving as reported by Ino et al.,[9] who worked at a pressure of $4\text{-}9\cdot10^{-5}$ torr, and by Jaunet and Sella,[32] who report a pressure of 10^{-6} torr, was not confirmed by Gillet et al.[31] working at 10^{-6} and 10^{-8} torr. Our own work in the 10^{-6} to 10^{-8} torr range confirms Gillet et al.'s[31] findings. We find that the

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(100) orientation on the vacuum-cleaved surface is always weaker than on the air-cleaved surface. This is illustrated in Fig. 2 which shows the early growth stages of Au deposited at $\sim$.5 Å/sec onto air- and vacuum-cleaved NaCl at 325°C in a vacuum of $2 \cdot 10^{-6}$ torr. A thick film obtained under similar conditions is epitaxial on the air-cleaved surface and predominantly (111) on the vacuum-cleaved surface. These discrepancies on vacuum-cleaved NaCl surfaces regarding the influence of the residual gas on the epitaxial temperature are, in our opinion, due to differences in residual gas pressure and composition. If we assume that the influence of the residual gas on the film orientation is determined by the relative arrival rate of "active" residual gas atoms to metal atoms then a comparison between different experiments at the same temperature is possible only for the same gas composition and the same p/r ratios. Here (r) is the deposition rate and (p) is the partial pressure of the active residual gas components, i.e., of those components which influence the film orientation (assumed to be H_2O and CO_2, so that $p \sim p_{total}$). Ino et al.[9] deposited at $r \sim$ .2 - 1 Å/sec, $p = 4 - 9 \cdot 10^{-5}$, so that at $p = 4 \cdot 10^{-6}$ torr, as used in our experiment, we have to use a rate $r < 4 \cdot 10^{-2}$ Å/sec. This is actually indicated by experiment: Au deposited at $r \sim$ .01 Å/sec at $p = 4 \cdot 10^{-6}$ torr formed (100) films on vacuum-cleaved NaCl at 325°C. Conversely, if the rate is kept constant the pressure has to be increased to obtain comparable conditions: an increase of p to about $5 \cdot 10^{-5}$ torr at $r \sim$ .5 Å/sec also produced a (100) Au film on vacuum-cleaved NaCl at 325°C. These observations suggest a reinterpretation of the observations of Harsdorff and Raether[33] who had explained the influence of the residual gas on the orientation of Ag films on vacuum-cleaved NaCl in terms of Harsdorff's multilayer adsorption model.[10] They find a strong

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dependence of the orientation perfection (at a given substrate temperature T) upon (p) and (r). Complete orientation at $T = 60°$, for example, is obtained for $r \sim 2$ Å/sec at $2 \cdot 10^{-4}$ torr and $r \sim .2$ Å/sec at $2 \cdot 10^{-5}$ torr, i.e., at a $p/r \sim 1 \cdot 10^{-4}$ torr sec/Å. For lower values of p/r the orientation perfection decreases rapidly. The results for both Ag and Au on NaCl indicate that in many vacuum systems (i.e., residual gas compositions) a $p/r \geq 1 \cdot 10^{-4}$ torr sec/Å is necessary to obtain the maximum lowering of the epitaxial temperature on a vacuum-cleaved surface.

It is not clear at present whether the residual gas promotes epitaxy by influencing the nucleation or the coalescence process, although the latter appears more likely. The mechanism by which the gas influences orientation is probably adsorption on the growing crystals and not on the NaCl surface. This can be deduced, at least as far as H_2O molecules are concerned, from the work of Bethge et al.[12] and Hucher et al.[13] according to which only negligible H_2O adsorption on NaCl occurs at such low pressures. The sticking coefficient of the residual gas must be very small or only a small fraction of the residual gas is active because at $p/r = 1 \cdot 10^{-4}$ torr sec/Å about 100 residual gas molecules arrive for each metal atom. The nature of the active gas is not certain, although H_2O and CO_2 are likely, and He, H_2,[33] dry N_2 and O_2[16] can be excluded. It is not even certain that the residual gas influences the film growth directly rather than indirectly via the vapor source (see Sec. VI). Obviously more work needs to be done to understand the process involved.

VI. IMPURITIES FROM THE VAPOR SOURCE

One of the obvious sources of impurities is the vapor source itself. These impurities may come from (a) the evaporating material, (b) the bulk

of the evaporator, or (c) they may be formed on the evaporator surface.
Even the purest metals available can contain significant amounts of impurities. For example, 99.9999% Au has been found to contain 50 p.p.m. Fe and Si, 10 p.p.m. Ca, Mg, Na, and K, and smaller amounts of many other elements.[34] The significance of the Na and K content will become clear below. The impurity content of the refractory metals which are in general used in resistance and electron bombardment heated evaporation sources is usually much higher. Of particular significance is again the alkali content. Finally, the interaction of the residual gas with the hot evaporator surface may produce impurities. O_2, H_2O, and CO_2 oxidize refractories with low carbon content and lead to the formation of oxides which are volatile at the temperatures used for the evaporation of many materials. The formation of volatile oxides may be of importance in the residual gas influence on epitaxy as discussed in Sec. V; however, no work has been done on this problem.

The major effect of impurities from the vapor source on the growth of single crystal films observed to date is not due to neutral atoms or molecules, but is caused by ions. Mihama and Tanaka[35] have reported a considerable improvement in film orientation by placing a screen at a high negative potential (< -1.5 kV) in the path of the vapor beam. They observed a lowering of the epitaxial temperature from Ino's et al.[9] 400°C to 300°C on an air-cleaved surface at p ∿ 10^{-5} torr and r ∿ .2 Å/sec. They concluded that both positive ions and an electric field on the crystal surface are necessary for the effect to occur.

We have extended Mihama and Tanaka's[35] measurements and confirmed their observation (see Fig. 3). Au was evaporated simultaneously onto a specimen without a screen and onto one with a 100-mesh W screen in the vapor path.

The screen was maintained at various potentials (V_s) and located 2 cm from the specimen surface. Evaporations were performed both in an unbaked system ($p = 2 \cdot 10^{-5}$, $2 \cdot 10^{-8}$ torr) and in a baked system ($p = 4 \cdot 10^{-9}$ torr) with $r \sim .1$ Å/sec onto air-cleaved NaCl at $T \sim 250°C$. At low voltages (± 90 V, -1.5 kV) no influence of the screen was observed, but at -2.5 kV the (100) became considerably stronger. Similarly, predominant (100) was obtained without a screen at high negative potential when an electron bombardment heated Mo Knudsen cell at $+1$ kV was used as an evaporator in place of the grounded resistance heated W source. Both results can be attributed to positive ion bombardment of the NaCl surface because many vapors of metals evaporated from resistance heated refractories in the 10^{-6} torr range in unbaked systems contain as many as one positive ion per $10^3 - 10^4$ neutral atoms.[36,37] These ions are accelerated and focused onto the substrate by the negatively charged screen. The ion current which passes the screen is decelerated between screen and specimen to energies of the order $V_s/10$ as estimated from the geometry. As the effect is observed only for $V_s \leq -2.5$kV, the ions have an energy of at least several hundred eV, which is considerably above the sputtering threshold. It appears likely that they influence the film growth in a manner similar to electron bombardment.

The ion effect discussed above is distinctly different from that observed by Chopra,[36] in which the application of an electric field parallel to the air-cleaved NaCl surface facilitated the coalescence in epitaxial Ag films and improved the orientation perfection. An explanation for the influence of these very low energy ions is suggested by a comparison of Chopra's[36] conductivity measurements with those of Kennedy et al.[37] The latter obtained the reduction in resistance at a given film thickness

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(earlier coalescence!) noted in Ag films on NaCl not only with (a) application of an electric field parallel to the surface, but also (b) by grounding the substrate, or (c) by deflecting the ion beam. Inasmuch as (a) and (b) remove the charge only, while (c) removes the whole ion, it appears that the earlier coalescence is due to the removal of positive charge from the growing film. This indicates that the charge associated with an ion tends to suppress early coalescence and reduce--in discontinuous films--the orientation perfection, while the surface damage associated with a sufficiently energetic ion improves the orientation perfection.

The ions definitely originate at the source, but can be produced there in a variety of ways. The positive ion emission from heated refractory metals and its enhancement by reactive residual gases has been known for some time,[38-40] but the currents are generally too low to be significant here. A second mechanism is surface ionization of atoms or molecules on the surface of the hot refractory metal (or of Au, see below). On most clean refractories only K, Rb, Cs, and certain of their compounds are ionized efficiently, while on oxygen covered refractories several other species are well ionized. Preliminary experiments indicate that this surface ionization process can contribute significantly to the total ion current and that the neutral species originates from surfaces in the environment of the vapor source and heated by it.

The most significant source of ions is the evaporating material itself. An ionizable impurity content of 10 p.p.m. produces an ion current (i_+) to vapor flux (i_o) ratio of $i_+/i_o = 10^{-5}$, provided that all impurity atoms are ionized at the surface and that the ion flux is proportional to the evaporation rate. If all ions were focused onto the substrate then with our

geometry--and also Mihama and Tanaka's[35]--an $i_+/i_o \sim 3 \cdot 10^{-3}$ could be

obtained. Al, Cu, and Ag have work functions ϕ of 4.17, 4.51, and 4.30 eV,

respectively,[41] so that of the known common impurities only K (ionization

E_i = 4.34 eV) can be ionized efficiently unless ionization occurs on an

oxidized refractory surface. However, for Au (ϕ = 5.22)[41] both K and

Na (E_i = 5.14 eV) are ionized efficiently. The emission of K^+ and Na^+

from hot Au has been demonstrated recently.[25] Our measurements indicate

a typical ion flux of $i_+ \sim 5 \cdot 10^9$ ion/cm^{2}sec at the substrate with a

deposition rate of .1 Å/sec ($i_o \sim 5 \cdot 10^{13}$ atoms/cm^{2}sec); this corresponds

to $i_+/i_o \sim 1 \cdot 10^{-4}$. These measurements were made under conditions that

produced the observed orientation effect (-2.5 kV screen, -200 V surface

potential). Thus, .01% of K^+ and Na^+ ions in the vapor can have a major

influence on the film growth.

In addition to the charge and energy effects of alkali ions their

chemical behavior can also modify the film growth significantly if a suffi-

cient number of them is present. This is demonstrated by the following

observations made with Au on NaCl (p = $4 \cdot 10^{-8}$, r $\sim$ 0.5 Å/sec, T = 300°C):

(1) Deposition of Au onto a vacuum-cleaved surface in the presence of a

low Na flux results in a (100) film under conditions which would lead to

(111) in the absence of Na; (2) Simultaneous deposition of Au and Na pro-

duces a thin epitaxial $NaAu_2$ film; (3) The controversial "5x1" superstructure

diffraction pattern of the Au (100) plane develops coincident with the depo-

sition of Na on a growing epitaxial film.

We conclude that alkali impurities originating at the source can influ-

ence the film growth via their charge (when ionized), via their energy (when

accelerated) and via their chemical reactivity (at sufficiently high flux).

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VII.   INFLUENCE OF THE ELECTRON BEAM

The fact that electron bombardment of an alkali halide substrate influences epitaxy has been known for some time.[5,7,42,43] Recently this phenomenon has been studied in more detail by Stirland[44] and in particular by Palmberg et al.[45] who have extended the investigation to low temperatures. Dr. Rhodin will discuss their results in the following paper. We will limit ourselves, therefore, to our own work at temperatures above 200°C, which was done in the UHV-RHEED system at electron energies between 10 and 20 kV and current densities of less than $1 \cdot 10^{-6}$ A/cm^2. Irradiation was done both shortly before and during deposition. The following effects are observed:[7] (1) Roughening of the alkali halide surface either by locally varying decomposition or by recondensation of material decomposed from the surface; (2) An increase in particle density in thin films and an increase of the surface coverage in thicker films; (3) A change in crystal orientation. In all cases electron irradiation prior or during the initial stages of deposition favored the formation of (100). Therefore, the effect is not so obvious in films which develop the (100) without irradiation, e.g., Au on air-cleaved NaCl, air- and vacuum-cleaved KCl. On vacuum-cleaved NaCl the beam area in a thick film is found to have perfect (100) with "1/5 streaks" while the unirradiated area has (111). The irradiated area of a Ag film deposited at 270°C onto KCl shows very good (100) while the rest of the film is very poorly oriented. Similarly, for Al deposited on NaCl at 270°C the film on the irradiated area is predominantly (100); and (4) Electron bombardment of a thin Au film deposited on air- or vacuum-cleaved NaCl produces epitaxial NaAu$_2$ (Fig. 4).

These experiments indicate that electron bombardment produces nucleation sites and free alkali which have considerable influence on the film formation process.

VIII.   DISCUSSION AND SUMMARY

In the preceding sections we have described a number of drastic film orientation changes caused by impurities. The impurities frequently lead to epitaxy under conditions which would produce (111) on the clean surface. Examples are (1) the influence of impurities in the surface layer (formed by air or water vapor exposure) on the growth of Au and Ag on NaCl, (2) the influence of the residual gas present during deposition on the growth of Cu, Ag, and Au films on NaCl, and (3) the influence of alkali ion and electron bombardment on the growth of Au on NaCl. However, impurities do not always cause a transition from a (111) to epitaxy as demonstrated by the influence of Ca doping on the growth of Au on air-cleaved NaCl.

Impurities influence both the nucleation and the coalescence process. In the nucleation process it is mainly the particle number which is increased with usually minor changes in the particle orientation. During coalescence the change in particle orientation is--sometimes strongly--modified by impurities.

It is difficult at the present time to select the basic parameters that are influenced most by specific impurities. We have to consider the following: (1) the thermal accommodation coefficient α of the hot vapor beam, (2) the heat of adsorption ΔH_a, (3) the activation energy for surface diffusion ΔH_d, (4) the absolute value and orientation dependence of the binding energy of atomic clusters, (5) the interfacial energy between film

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crystal and substrate, (6) the absolute value and anisotropy of the surface energy σ_{hkl} of the film crystal, (7) the surface energies σ_s of the substrate, and (8) the defect nature, density, and distribution on the substrate surface. There is little doubt that all of these parameters except perhaps α can be changed considerably by impurities. This makes the separation of the influence of individual parameters difficult. In order to obtain a reliable understanding of the elementary processes involved in the influence of impurities on the film growth we have to know much more about the impurity influence on the individual parameters, for example: (1) the influence of alkalis on the anisotropy of the surface energy of Au, (2) the change of the surface energy of f.c.c. metals by adsorption of H_2O, CO_2, or other gases, and (3) the chemical composition of air-exposed alkali halide surfaces. With this knowledge and the use of controlled impurities, we should then be able to separate the influence of impurities on other parameters such as ΔH_a or ΔH_d by detailed quantitative studies of the growth of thin films.

In conclusion, we have demonstrated (1) that specific impurities produce specific changes in the formation processes of thin films, and (2) that most of the existing discrepancies can be eliminated if these impurity effects are properly taken into account.

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FIGURE CAPTIONS

Fig. 1. Au film ∿ 5 Å thick, deposited on air-cleaved surfaces of Ca-doped

(.2 mole percent) and undoped NaCl, (p = 2·10^{-8}, r ∿ .5 Å/sec,

T = 340°C). (a) TED-doped substrate, (b) corresponding TEM, X30,000,

(c) TED-undoped substrate, (d) corresponding TEM, X30,000.

Fig. 2. Au film ∿ 5 Å thick, deposited on NaCl, (p = 2·10^{-6}, r = .5 Å/sec,

T = 330°C). (a) TED air-cleaved surface, (b) corresponding TEM,

X30,000, (c) TED vacuum-cleaved surface, (d) corresponding TEM,

X30,000.

Fig. 3. Au deposited simultaneously on NaCl, with and without -2.5 kV screen

in vapor path (p = 4·10^{-9}, r = .1 Å/sec, T ∿ 250°C, (a) TED with

screen, (b) corresponding TEM, X30,000, (c) TED without screen,

(d) corresponding TEM, X30,000.

Fig. 4. UHV-RHEED patterns showing the development of (100) NaAu$_2$ by electron

bombardment of a thin Au film at 330°C. (a) (100) Au with NaCl

streak pattern, (b) first NaAu$_2$ spots, (c) intense NaAu$_2$ pattern,

⟨110⟩ azimuth, (d) ⟨100⟩ azimuth NaAu$_2$ pattern.

TABLE I
Residual Gas Composition

Mass No.	Unbaked System Total Press. $= 3.3 \cdot 10^{-7}$	Baked System Total Press. $= 3.3 \cdot 10^{-10}$
2	9	43
16	3	5
17	16	< .5
18	60	< .5
28	3	34
44	2	15

Typical relative peak heights of the residual gas with mass numbers less than 50 in an ion-pumped all stainless steel system. Measured by a Varian Quadrupole RGA. Several mass numbers (1, 4, 12, 13, 14, 15, 20, 22, 26, and 32) were detected in the unbaked system with relative peak height <1.

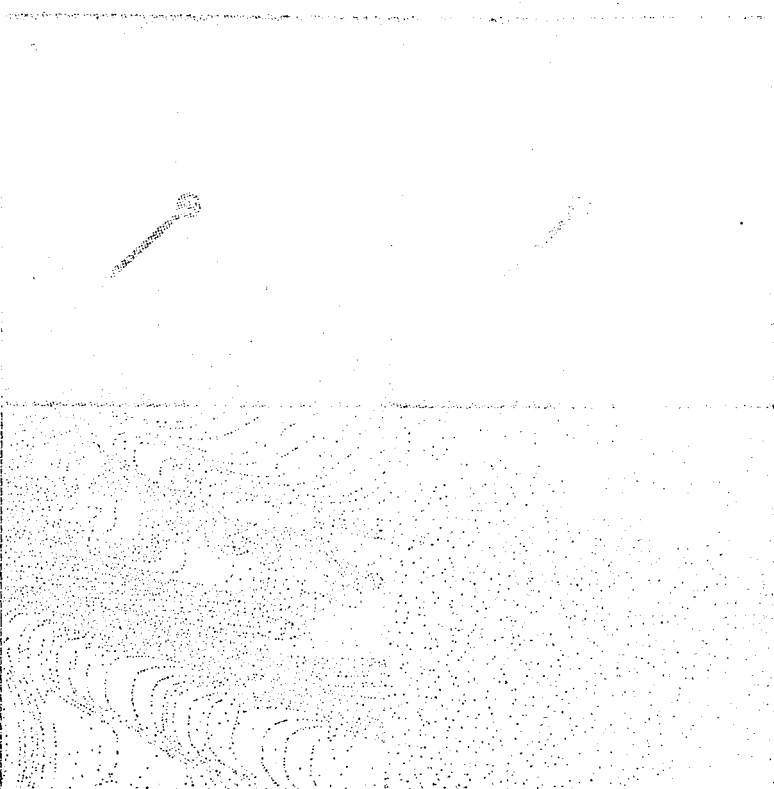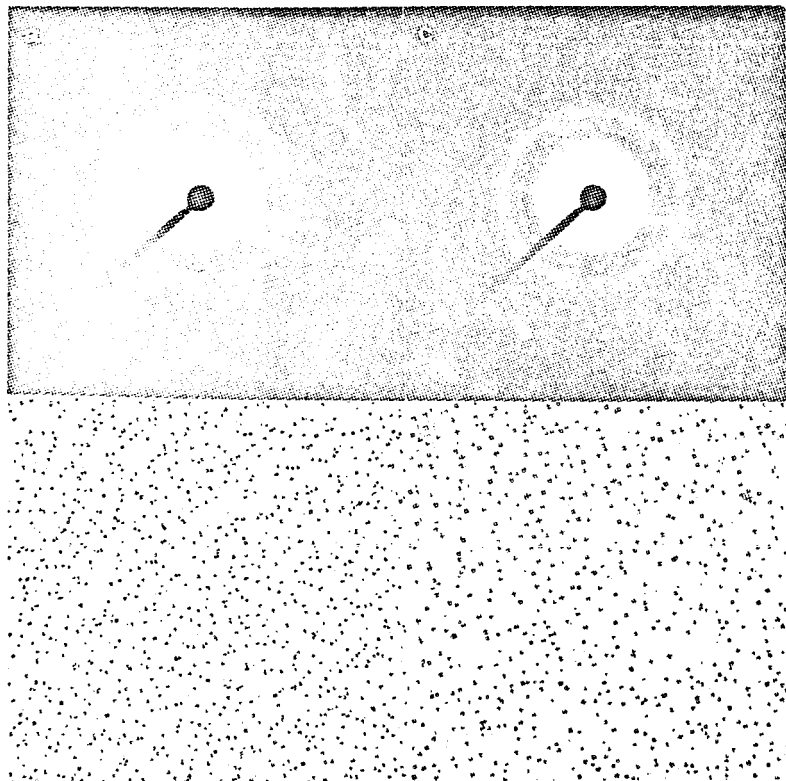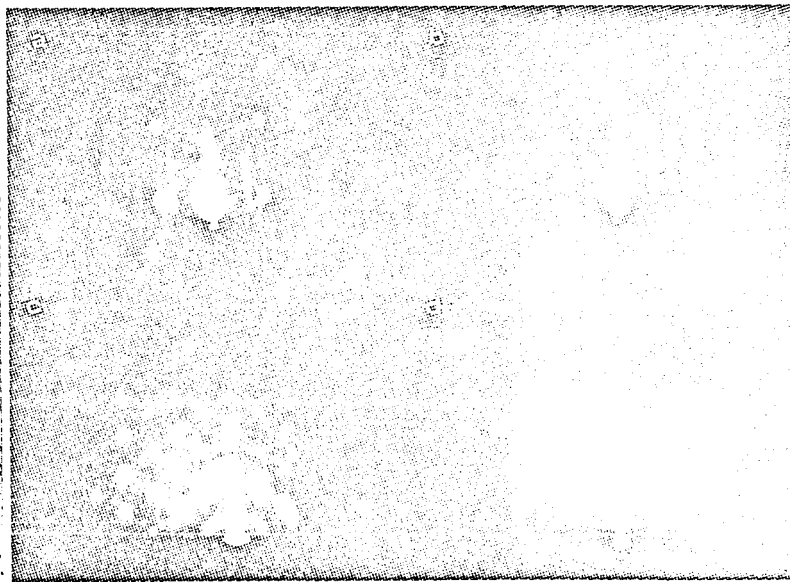FIG. 1

FIG. 2

FIG. 3

FIG. 4